

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 10-195404

(43)Date of publication of application : 28.07.1998

(51)Int.Cl.

C09J 11/00

B41J 2/01

B41M 5/00

(21)Application number : 09-249119

(71)Applicant : SEIKO EPSON CORP

(22)Date of filing : 12.09.1997

(72)Inventor : KATO SHINICHI
TAKEMOTO KIYOHICO
KUBOTA KAZUhide

(30)Priority

Priority number : 08256932
08302227Priority date : 27.09.1996
13.11.1996

Priority country : JP

JP

(54) INK JET RECORDING

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a method for recording with an ink jet, comprising printing with a recording medium using a reacting solution and an ink composition, and enabling to give good images.

SOLUTION: This method for recording with an ink jet comprises using an ink composition containing a coloring agent, a resin emulsion, etc., and a reacting solution containing a reacting agent, such as a polyvalent metal salt or a polyallyl amine, capable of reacting with the components such as the coloring agent and the resin emulsion to produce an aggregation. Therein, the reacting solution and the ink composition each has a surface tension of <40mN/m. In order to realize the surface tension, an anionic surfactant such as a sodium polyoxyethylene alkyl ether sulfate is used.

LEGAL STATUS

[Date of request for examination] 10.08.2001

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.**** shows the word which can not be translated.

3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] The are ink-jet record method of printing by making reaction mixture and ink constituent containing reaction agent adhering to record medium, and using both things of less than 40 mN/m as aforementioned reaction mixture and aforementioned ink constituent ink-jet [surface tension / the] record method.

[Claim 2] The ink-jet record method according to claim 1 which is that to which the aforementioned reaction agent contacts the aforementioned ink constituent, and generates an aggregate.

[Claim 3] The ink-jet record method according to claim 1 or 2 that the aforementioned reaction agent is polyvalent metallic salt, the poly allylamine, or its derivative.

[Claim 4] The ink-jet record method given in any 1 term of claims 1-3 which is that to which the aforementioned ink constituent uses a pigment as a coloring agent.

[Claim 5] The ink-jet record method given in any 1 term of claims 1-4 which is the thing in which the aforementioned ink constituent comes to contain a resin emulsion and/or inorganic-oxide colloid.

[Claim 6] The ink-jet record method given in any 1 term of claims 1-5 whose aforementioned inorganic-oxide colloid is colloidal silica.

[Claim 7] The ink-jet record method given in any 1 term of claims 1-6 which is the thing in which the aforementioned ink constituent comes to contain the anionic surfactant which has a polyoxyethylene machine.

[Claim 8] The ink-jet record method given in any 1 term of claims 1-7 whose aforementioned anionic surfactant is a polyoxyethylene-alkyl-ether sulfate or a polyoxyethylene phenyl-ether sulfate.

[Claim 9] The ink-jet record method given in any 1 term of claims 1-8 whose aforementioned anionic surfactant is the sodium salt of a polyoxyethylene-alkyl-ether sulfate, or sodium salt of a polyoxyethylene phenyl-ether sulfate.

[Claim 10] The ink-jet record method given in any 1 term of claims 1-9 whose sodium salt of the aforementioned polyoxyethylene-alkyl-ether sulfate is what is expressed with the following formula (V).

$\text{RO}(\text{CH}_2 \text{ CH}_2 \text{ O})_n \text{SO}_3 \text{Na}$ (V)

(R expresses an alkyl group among a formula and n expresses the integer of 1-50)

[Claim 11] The record object by which printing was carried out to any 1 term of claims 1-10 by the ink-jet record method of a publication.

[Translation done.]

[Date of extinction of right]

Copyright (C); 1998,2003 Japan Patent Office

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.*** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

Background of the Invention]

The field this invention of invention relates to the ink-jet record method of printing by making reaction mixture and an ink constituent adhering to a record medium, in detail about the ink-jet record method.

[0002] The background technical ink-jet record method is the printing method which the globule of an ink constituent is made to fly and prints by making it adhere to record media, such as paper. This method has the feature [picture / high-definition / high resolution and] that it can print at high speed, with comparatively cheap equipment. Usually, as for the ink constituent used for ink-jet record, what made water the principal component and contained wetting agents, such as a glycerol, for the purpose, such as a coloring component and blinding prevention, in this is common.

[0003] On the other hand, as the ink-jet record method, newly, after applying a polyvalent-metallic-salt solution to a record medium, the method of applying the ink constituent containing the color which has at least one carboxyl group is proposed recently (for example, JP.5-202328.A). In this method, it is supposed that the high-definition picture which insoluble complex is formed from polyvalent metal ion and a color, and has water resistance by existence of this complex, and does not have color bleeding can be acquired.

[0004] Moreover, the proposal that the high-definition color picture which does not have color bleeding highly [picture concentration] is obtained is also made by using it combining the color ink containing the surfactant or permeability solvent, and salt which give permeability at least, and the black ink thickened or condensed by operation with this salt (JP.6-106735.A). That is, the ink-jet record method to which it is supposed that a good picture is acquired by printing the first liquid containing the salt and 2 liquid with an ink constituent is proposed.

[0005] Moreover, the ink-jet record method of in addition to this printing 2 liquid is proposed (for example, JP.3-240557.A, JP.3-240558.A).

[0006]

[Summary of the Invention] In the ink-jet record method of printing such 2 liquid this time, this invention person etc. is making both surface tension of reaction mixture and an ink constituent into less than 40 mN/m, and acquired knowledge that good printing is realizable, this invention is based on this knowledge.

[0007] Therefore, this invention sets offer of a method which can realize a good picture as the purpose in the ink-jet record method of printing 2 liquid.

[0008] and the thing [surface tension / the] which prints by the ink-jet record method by this invention making the reaction mixture and the ink constituent containing the reaction agent adhere to a record medium are the ink-jet record method and using both the things of less than 40 mN/m as the aforementioned reaction mixture and the aforementioned ink constituent — it comes out

[0009]

[Detailed Description of the Invention]

The ink-jet record method by the ink-jet record method this invention comes to contain in a record medium the process which prints reaction mixture and an ink constituent. And if it is in this invention, the surface tension uses [both] the thing of less than 40 mN/m as reaction mixture and an ink constituent. That is, if it is in this invention, surface tension uses extremely wettability reaction mixture and ink constituent of less than 40 mN/m which are good, namely, are easy to permeate a record medium. According to this invention, even if it uses the high ink constituent of the permeability considered to be easy to permeate generally, a little ink advantage at the time of using the high ink constituent of permeability by one side, i.e., quick-drying [of printing]. Furthermore, an advantage that the coloring nature of printing is good according to this invention and a quality picture with little bleeding is acquired is enjoyable. Consumption of ink can be lessened as a result of the dot of a big path being realizable especially with a little ink constituent. Furthermore, generating of the wrinkling in paper can be reduced especially from the thing for which the amount of ink adhering to a record medium can be made small.

[0010] Surface tension of the above-mentioned reaction mixture and an ink constituent may be realized by the addition of a penetrating agent which carries out a postscript. In this invention, the postscript of the detail of the penetrating agent which can be used is carried out.

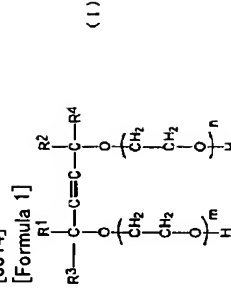
[0011] If it is in the record method using 2 liquid like the ink-jet record method by this invention, good printing is realizable because reaction mixture and an ink constituent contact. That is, when reaction mixture and an ink constituent contact, the reaction agent in reaction mixture destroys the distributed state of the component of the pigment and others in an ink constituent, and makes it condense. It adheres on a record medium, and with the high depth of shade, it bleeds and this aggregate is considered to realize few printing of nonuniformity. Furthermore, in a color picture, it also has an advantage that it can prevent effectively, the uneven color mixture, i.e., the color bleeding, in the border area of a different color.

[0012] As for the reaction mixture by the reaction mixture this invention, it comes to make less than 40 mN/m of the surface tension into 35 or less mN/m more preferably 38 or less mN/m. According to the desirable mode of this invention, this surface tension may be realized by addition of a penetrating agent. In this invention as a penetrating agent which can be used An

anionic surfactant, Various surfactants, such as a cation nature surfactant, a nonionic surfactant, and an amphoteric surface active agent, Alcohols, such as a methanol, ethanol, and iso-propyl alcohol, An ethylene glycol monomethyl ether, a diethylene glycol monoethyl ether, The low-grade alkyl ether of polyhydric alcohol, such as the diethylene-glycol monobutyl ether, the triethylene-glycol monobutyl ether, the propylene-glycol monobutyl ether, and the dipropylene-glycol monobutyl ether, etc. is raised.

[0013] According to the mode with a still more desirable this invention, it is desirable to use the compound expressed with the following formula (I) and/or the lower-alcohol ether of polyhydric alcohol as a penetrating agent.

[0014]



(The inside of a formula, 0 < m+n <= 50, R¹, R², R³, and R⁴ are alkyl groups independently) There are specifically ORUFINY, SAFI Norian 82, SAFI Norian 440, SAFI Norian 465, SAFI Norian 485 (all manufacture : Air Products and Chemicals, Inc.), etc. as a typical thing of a compound expressed with a formula (I). These are independent or may be added two or more kinds.

[0015] The reaction mixture used in this invention comes to contain the reaction agent which contacts an ink constituent and generates an aggregate. An aggregate is considered that a reaction agent and the coloring agent component in an ink constituent react, and are formed. Furthermore, although a resin emulsion and/or inorganic-oxide colloid can be included if it is in this invention so that a postscript may be carried out, as for a reaction agent, it is desirable according to the desirable mode of this invention that it is what collapses the dissolution of this resin emulsion and inorganic-oxide colloid and/or a distributed state.

[0016] Although it will not be limited if the reaction agent used in this invention has the above-mentioned property, as the desirable example, polyvalent metallic salt, the poly allylamine, or its derivative is mentioned.

[0017] The polyvalent metallic salt as a reaction agent consists of anions combined with the polyvalent metal ion and these polyvalent metal ion more than bivalent, and is meltable in water. As an example of polyvalent metal ion, trivalent metal ion, such as divalent-metal ion aluminum³, such as calcium²⁺, Cu²⁺, nickel²⁺, Mg²⁺, Zn²⁺, and Ba²⁺, and Fe³⁺, and Cr³⁺, is raised, as an anion -- Cl⁻, NO₃⁻, I⁻, Br⁻, ClO₃⁻, and CH₃ COO⁻ etc. -- it is raised

[0018] The metal salt which consists of calcium²⁺ or Mg²⁺ especially gives a suitable result from two viewpoints of pH of reaction mixture, and the quality of the printed matter obtained.

[0019] Although the concentration in the reaction mixture of these polyvalent metallic salt may be suitably determined in the range from which a quality of printed character and the effect which is blinding prevention are acquired, it is about 0.1 - 40 % of the weight preferably, and is about 5 - 25 % of the weight more preferably

[0020] According to the desirable mode of this invention, polyvalent metallic salt consists of polyvalent metal ion more than bivalent, and the nitrate ion or carboxylic-acid ion combined with these polyvalent metal ion, and it is desirable that it is meltable in water.

[0021] Here, carboxylic-acid ion is preferably guided from the saturated-fat group monocarboxylic acid of carbon numbers 1-6, or the ring formula monocarboxylic acid of carbon numbers 7-11. As a desirable example of the saturated-fat group monocarboxylic acid of carbon numbers 1-6, formic acid, an acetic acid, a propionic acid, butanoic acid, an isobutyric acid, a valeric acid, an isovaleric acid, a pivalic acid, a hexanoic acid, etc. are mentioned. Especially formic acid and an acetic acid are desirable.

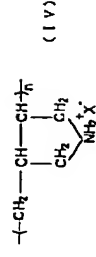
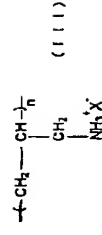
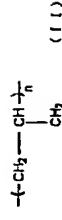
[0022] The hydrogen atom on the saturated-aliphatic-hydrocarbon machine of this monocarboxylic acid may be replaced by the hydroxyl group, and a lactic acid is mentioned as a desirable example of such a carboxylic acid.

[0023] Furthermore, as a desirable example of the ring formula monocarboxylic acid of carbon numbers 6-10, a benzoic acid, a naphthoic acid, etc. are mentioned and it is a benzoic acid more preferably.

[0024] Moreover, the poly allylamine and the poly allylamine derivative as a reaction agent are meltable in water, and are a cation system macromolecule which carries out an electric charge to plus under water. For example, a formula (II), a formula (III), and a ceremony (IV) are held.

[0025]

[Formula 2]



(X- expresses a chloride ion, a bromide ion, iodide ion, a nitrate ion, a phosphate anion, a sulfate ion, acetic-acid ion, etc. among a formula)

The copolymer of polymer and diaryl methylammonium chloride which the allylamine and the diarylamine copolymerized besides these, and a sulfur dioxide can also be used.

[0026] As for the content of these poly allylamine and the poly allylamine derivative, it is desirable that it is 0.5 - 10% of the weight of reaction mixture.

[0027] According to the desirable mode of this invention, in addition to polyvalent metallic salt, reaction mixture comes to contain a polyol. Here, the vapor pressure in 20 degrees C of this polyol is 0.01 or less mmHg, and the addition is preferably set to 1.0-5.0 one or more by the weight ratio to polyvalent metallic salt. According to the mode with a still more desirable this invention, the addition to the reaction mixture of this polyol is about 10 - 30 % of the weight preferably [that is 10 % of the weight or more] and more preferably.

[0028] As a desirable example of a polyol, polyhydric-alcohol, for example, glycerol, diethylene-glycol, triethylene-glycol, 1,5-pentanediol, 1, and 4-butanediol etc. is mentioned. Furthermore, as a desirable example of a polyol, sugar, for example, a monosaccharide, a disaccharide, oligosaccharide (a trisaccharide and a tetrasaccharide are included), and polysaccharide are raised, and a glucose, a mannose, a fructose, a ribose, a xylose, arabinose, a galactose, an aldonic acid, a GURUSHI seal, a sorbitol, a maltose, a cellobiose, a lactose, a sucrose, a trehalose, a maltotriose, etc. are raised preferably.

[0029] These polyols may be added as two or more mixture, even if added independently. When added as two or more mixture, the addition is made or more into one by the weight ratio to polyvalent metallic salt as the sum total.

[0030] According to the desirable mode of this invention, reaction mixture comes to contain the wetting agent which consists of a high-boiling point organic solvent. A high-boiling point organic solvent prevents the blinding of a head by preventing dryness of reaction mixture. As a desirable example of a high-boiling point organic solvent, although it laps also with the aforementioned polyol in part Ethylene glycol, a diethylene glycol, a triethylene glycol, A polyethylene glycol, a polypropylene glycol, a propylene glycol, A butylene glycol, 1 and 2, 6-hexane triol, a thioglycol, Polyhydric alcohol, such as a hexylene glycol, a glycerol, trimethylolmethane, and a trimethylol propane; Ethylene glycol monoethyl ether, An ethylene glycol monobutyl ether, the diethylene-glycol monomethyl ether, A diethylene glycol monoethyl ether, the diethylene-glycol monobutyl ether, The TORIECHIEREN glycol monomethyl ether, the triethylene-glycol monoethyl ether, The alkyl ether of polyhydric alcohol, such as the triethylene-glycol monobutyl ether, a urea, 2-pyrrolidone, a N-methyl-2-pyrrolidone, 1, 3-dimethyl-2-imidazolidinone, a triethanolamine, etc. are raised.

[0031] Although especially the addition of a high-boiling point organic solvent is not limited, it is about 0.5 - 40 % of the weight preferably, and is about 2 - 20 % of the weight more preferably.

[0032] According to the desirable mode of this invention, reaction mixture comes to contain the

low-boiling point organic solvent. As a desirable example of the low-boiling point organic solvent, a methanol, ethanol, n-propyl alcohol, iso-propyl alcohol, n-butanol, a sec-butanol, a tert-butanol, an iso-butanol, n-pentanol, etc. are raised. Especially monohydric alcohol is desirable. The low-boiling point organic solvent has the effect which shortens the drying time of ink. The addition of the low-boiling point organic solvent has 0.5 – 10 desirable % of the weight, and it is 1.5 – 6% of the weight of a range more preferably.

[0033] According to the desirable mode of this invention, reaction mixture comes to contain a triethanolamine for pH adjustment. When a triethanolamine is added, the addition has about 0 – 2.0 desirable % of the weight.

[0034] Moreover, the color coloring agent indicated by the term of the after-mentioned ink constituent should be added, it should be colored, and this reaction mixture should have the function of an ink constituent.

[0035] As for the ink constituent used in an ink constituent this invention, it comes to make less than 40 mN/m of the surface tension into 35 or less mN/m more preferably 38 or less mN/m. According to the desirable mode of this invention, this surface tension may be realized by addition of a penetrating agent, and the thing same as an example of the penetrating agent which can be used as the penetrating agent used for the above-mentioned reaction mixture is mentioned.

[0036] Furthermore, according to the desirable mode of this invention, it is desirable to use an anionic surfactant as a penetrating agent contained in the ink constituent used in this invention. The ink constituent which comes to contain an anionic surfactant, and the ink constituent which comes to contain the compound of the formula (V) which especially carries out a postscript are excellent in preservation stability, and has the big penetrating power to the record medium.

According to the constituent which contains an anionic surfactant especially with the latter property, the pixel (specifically dot) of a big path is realizable with a little ink constituent. Moreover, an anionic surfactant hardly affects the reaction of the reaction agent in reaction mixture, and the component in an ink constituent. Therefore, the advantage of not barring realization of a picture with little bleeding which is the feature of the ink-jet record method using 2 liquid is also acquired.

[0037] As a desirable example of an anionic surfactant Fatty-acid soap, N-acyl-N-methyl glycine salt N-acyl-N-methyl-beta-alanine salt, A N-acyl glutamate, an alkyl ether carboxylate, an acyl peptide, An alkyl sulfonate, alkylbenzene sulfonates, alkylnaphthalenesulfonate, A naphthalene sulfonate formalin polycondensation object, a dialkyl sulfoacetate, Alkyl sulfoacetate, alpha-olefin sulfonate, N-acyl methyl taurine, Sulfated oil, a higher-alcohol sulfate salt, the second class higher-alcohol sulfate salt, Alkyl ether sulfate, the second class higher-alcohol ethoxy sulfate, A polyoxyethylene-alkyl-ether sulfate, a polyoxyethylene-alkyl-phenyl-ether sulfate, MONOGURI sulfate, a fatty-acid ARUKI roll amidosulfuric-acid ester salt, alkyl ether phosphate, an alkyl phosphate, etc. are raised.

[0038] Moreover, according to the more desirable mode of this invention, use of the sodium salt of the polyoxyethylene-alkyl-ether sulfate expressed especially with the following formula (V) is desirable.

[0039]

$\text{RO}(\text{CH}_2 \text{ CH}_2 \text{ O})_n \text{ SO}_3 \text{ Na (V)}$

(the inside of a formula, and R --- an alkyl group --- expressing the alkyl group of a straight chain or the branched-chain carbon numbers 1–30 preferably, n expresses the integer of 1–50)

[0040] There is specifically high tenor 325D (available from Dai-ichi Kogyo Seiyaku Co., Ltd.) as a typical thing of a compound expressed with a formula (V).

[0041] From a waterproof viewpoint of the picture acquired, the addition of an anionic surfactant is 0.01 – 5.0% of the weight of a range preferably, and is 0.1 – 2 % of the weight more preferably.

[0042] The ink constituent used in this invention comes to contain a coloring agent and water at least.

[0043] It is desirable that it is what reacts with said reaction agent as a coloring agent contained in the ink constituent used in this invention, and forms an aggregate. Moreover, a pigment is desirable although coloring agents may be any of a color and a pigment.

[0044] As a color, various colors usually used for ink-jet record, such as direct dye, acid dye, the food color, basic dye, a reactive dye, a disperse dye, a vat dye, a solubilized vat dye, and a reaction disperse dye, can be used.

[0045] Moreover, an inorganic pigment and an organic pigment can be used without a special limit as a pigment. In addition to titanium oxide and an iron oxide, as an inorganic pigment, the carbon black manufactured by well-known methods, such as the contacting method, the-furnace method, and thermal **, can be used. Moreover, as an organic pigment, an azo pigment (an azo lake, insoluble azo pigment, a disazo condensation pigment, a chelate azo pigment, etc. are included), polycyclic formula pigments (for example, phthalocyanine-pigment, perylene pigment, and peri non a pigment, an anthraquinone pigment, a Quinacridone pigment, a diazoxine pigment, a thioindigo pigment, an isoidolinone pigment, a kino FURARON pigment, etc.), color chelates (for example, a basic dye type chelate, an acid-dye type chelate, etc.), a nitro pigment, an oximido pigment, an aniline black

[0046] As for these pigments, according to the desirable mode of this invention, it is desirable to be added by ink as pigment dispersion liquid which were distributed in the aqueous medium and obtained with the dispersant or the surfactant. The dispersant commonly used as a desirable dispersant although pigment dispersion liquid are prepared, for example, a macromolecule contained in these pigment dispersion liquid will function also as the dispersant and surfactant of an ink constituent will be clear to this contractor.

[0047] The addition of the pigment to ink has about 0.5 – 25 desirable % of the weight, and it is about 2 – 15 % of the weight more preferably.

[0048] As for an ink constituent, according to the desirable mode of this invention, it is desirable to come to contain a resin emulsion. Here, a continuous phase is water and a resin emulsion means the emulsion whose dispersed phases are the following resinous principles. As a resinous principle of a dispersed phase, an acrylic resin, a vinyl acetate system resin, a styrene-butadiene system resin, a vinyl chloride system resin, an acrylic-styrene resin, a butadiene system resin, a styrene resin, bridge formation acrylic resin, bridge formation styrene resin, a benzoguanamine resin, phenol resin, silicone resin, an epoxy resin, etc. are raised.

[0049] As for this resin, according to the desirable mode of this invention, it is desirable that it is a polymer having a hydrophilic portion and a hydrophobic portion. Moreover, although it is not limited especially as long as the particle diameter of these resinous principles forms an emulsion, about 150nm or less is desirable, and is about 5–100nm more preferably.

[0050] These resin emulsions can be obtained by carrying out the distributed polymerization of the resin monomer underwater with a surfactant by the case. For example, the emulsion of an acrylic resin or a styrene-acrylic resin can be obtained by carrying out the distributed polymerization of an acrylic ester (meta) or (meta) an acrylic ester, and the styrene underwater with a surfactant. As for the rate of mixture with a resinous principle and a surfactant, it is desirable to usually carry out to 10:1 to about 5:1. The water resistance of better ink and permeability are acquired because the amount of the surfactant used is in the aforementioned range, although especially a surfactant is not limited --- as a desirable example --- an anionic surfactant (for example, dodecyl BENZERU sulfonic-acid sodium ---) The ammonium salt of lauryl acid sodium and polyoxyethylene-alkyl-ether sulfate etc., a nonionic surfactant (for example, polyoxyethylene alkyl ether ---) Polyoxyethylene alkyl ester, polyoxyethylene sorbitan fatty acid ester, Polyoxyethylene alkyl phenyl ether, polyoxyethylene alkylamine, polyoxyethylene alkylamide, etc. are raised, independent or two sorts or more can be mixed, and these can be used. Moreover, it is also possible to use an acetylene glycol (for them to be SAFI Norians 82,

104, 440, 465, and 485 (for all to be the products made from Air Products and Chemicals Inc.) to Olefin Y and a row).

[0051] moreover, the rate of the resin as a dispersed phase component, and water --- the resin 100 weight section --- receiving --- water 60 – the 400 weight sections --- the range of 100–200 is preferably suitable

[0052] It is also possible to use a well-known resin emulsion as such a resin emulsion, for example, the resin emulsion of a publication can be used for JP.62-1426B, JP.3-56573A, JP.3-

79678 A, JP 3-160068 A, JP 4-18462 A, etc. as it is.

[0053] moreover, the thing for which a commercial resin emulsion is used — possible — the micro gel E-1002 and E-5002 (a styrene-acrylic resin emulsion —) [for example,] the Nippon Paint Co., Ltd. make and BONKOTO 4001 (an acrylic resin emulsion —) BONKOTO 5454 (a styrene-acrylic resin emulsion —) by Dainippon Ink & Chemicals, Inc. The Dainippon Ink & Chemicals, Inc. make, SAE-1014 (a styrene-acrylic resin emulsion, Nippon Zeon Co., Ltd. make), SAIBI Norian SK-200 (an acrylic resin emulsion, SAIDEN CHEMICAL INDUSTRY CO., LTD. make), etc. are raised.

[0054] The ink used for this invention is 1 – 25% of the weight of a range preferably [containing a resin emulsion so that the resinous principle may become 0.1 – 40% of the weight of ink], and more preferably.

[0055] According to an interaction with the derivative of a reaction agent especially polyvalent metal ion, the poly allylamine, or the poly allylamine, a resin emulsion suppresses osmosis of a coloring component and has the effect which promotes fixing to a record medium further.

Moreover, depending on the kind of resin emulsion, a coat is formed on a record medium, and it also has the effect which also raises the scuff resistance of printed matter.

[0056] As for an ink constituent, according to the desirable mode of this invention, it is desirable to come to contain the thermoplastics of a resin emulsion gestalt. here, 50 degrees C – 250 degrees C of thermoplastics of softening temperatures are 60 degrees C – 200 degrees C and ** preferably Here, the word of a softening temperature shall mean low temperature most among the minimum film forming temperature (MFT), when it is in the gestalt of the temperature and the pour point where the glass transition point of thermoplastics, the melting point, and coefficient of viscosity become 1011–1012P, and a resin emulsion. In the heating process of the method by this invention, a record medium is heated at the temperature more than the softening temperature of thermoplastics.

[0057] Moreover, when it is heated more than softening or melting temperature and is cooled, as for these resins, what forms a film with firm water resistance and scuff resistance is desirable.

[0058] As an example of the thermoplastics of water-insoluble nature, a polyacrylic acid, the poly methacrylic acid, Poly methacrylic-acid ester, a poly ethyl acrylic acid, a styrene-butadiene copolymer, A polybutadiene, an acrylonitrile-butadiene copolymer, a chloroprene copolymer, A fluororesin, a fluoride vinylidene, polyolefin resin, a cellulose, a styrene-acrylic-acid copolymer, a styrene-methacrylic-acid copolymer, A polystyrene and styrene-acrylamide copolymer, poly isobutyl acrylate, A polyacrylonitrile, polyvinyl acetate, a polyvinyl acetal, a polyamide, A rosin system resin, polyethylene, a polycarbonate, a vinylidene chloride resin, Although a cellulose system resin, a vinyl acetate resin, an ethylene vinylacetate copolymer, a vinyl acetate-acrylic copolymer, vinyl chloride resin, polyurethane, a rosin ester, etc. are mentioned, it is not limited to these.

[0059] As an example of the thermoplastics of low molecular weight, animals-and-plants system waxes, such as a polyethylene wax, a montan wax, an alcoholic wax, a synthetic oxidation wax, an alpha olefin-maleic-anhydride copolymer, and carnauba wax, lanolin, paraffin wax, a micro crystalline wax, etc. are mentioned.

[0060] Moreover, the ink constituent used for this invention may contain inorganic-oxide colloid. Colloidal silica and alumina colloid are raised as a desirable example of inorganic-oxide colloid. these — general — SiO₂ and aluminum₂O₃ etc. — it is the colloidal solution which distributed the ultrafine particle in water or the organic solvent as the inorganic-oxide colloid marketed — a dispersion medium — water, a methanol, n-propanol, a xylene, etc. — it is — SiO₂ and aluminum₂O₃ etc. — that whose particle size of a particle is 5–100nm is common Moreover, pH of the inorganic-oxide colloidal solution has not a neutral region but many things currently prepared acid or alkaline. This is because the stable distribution field of inorganic-oxide colloid exists in an acidity and alkalinity side, and when adding to an ink constituent, it is necessary to add it in consideration of pH of the stable distribution field of inorganic-oxide colloid, and pH of ink.

[0061] As for the addition of the inorganic-oxide colloid in an ink constituent, it is desirable to add so that it may become 0.1 – 15 % of the weight, and two or more sorts of addition is also

possible for it.

[0062] As for an ink constituent, according to the desirable mode of this invention, it is desirable to come to contain an alginic-acid derivative. As a desirable example of an alginic-acid derivative, an alginic-acid alkali-metal salt (for example, sodium salt, potassium salt) alginic-acid-organic salt (for example, triethanolamine salt), an ammonium-alginate salt, etc. are mentioned.

[0063] The addition to the ink constituent of this alginic-acid derivative is about 0.01 – 1 % of the weight preferably, and is about 0.05 – 0.5 % of the weight more preferably.

[0064] Although why a good picture is acquired by addition of an alginic-acid derivative cannot be decided, the polyvalent metallic salt which exists in reaction mixture reacts with the alginic-acid derivative in an ink constituent, the distributed state of a coloring agent is changed, and it is thought that it originates in fixing to the record medium of a coloring agent being promoted.

[0065] As for an ink constituent, according to the desirable mode of this invention, it is desirable to come to contain an organic solvent. This organic solvent is a low-boiling point organic solvent preferably, and a methanol, ethanol, n-propyl alcohol, iso-propyl alcohol, n-butanol, a sec-butanol, a tert-butanol, an iso-butanol, n-pentanol, etc. are raised as the desirable example.

Especially monohydric alcohol is desirable. The low-boiling point organic solvent has the effect which shortens the drying time of ink.

[0066] Moreover, according to the desirable mode of this invention, the ink constituent used for this invention has a desirable bird clapper including the wetting agent which consists of a high-boiling point organic solvent further. As a desirable example of a high-boiling point organic-solvent agent, ethylene glycol, a diethylene glycol, A triethylene glycol, a polyethylene glycol, a polypropylene glycol, A propylene glycol, a butylene glycol, 1 and 2, 6-hexane triol, A thioglycol, a hexylene glycol, a glycerol, trimethylolethane, Polyhydric alcohol, such as a trimethylol propane, ethylene glycol monoethyl ether, An ethylene glycol monobutyl ether, the diethylene-glycol monomethyl ether, A diethylene glycol monoethyl ether, the triethylene-glycol monobutyl ether, The alkyl ether of polyhydric alcohol, such as the triethylene-glycol monobutyl ether, a urea, 2-pyrrolidone, a N-methyl-2-pyrrolidone, 1, 3-dimethyl-2-imidazolidinone, a triethanolamine, etc. are raised.

[0067] 0.5 – 40% of the weight of the ink of the addition of these wetting agents is desirable, and it is 2 – 20% of the weight of a range more preferably. Moreover, 0.5 – 10% of the weight of the ink of the addition of the low-boiling point organic solvent is desirable, and it is 1.5 – 6% of the weight of a range more preferably.

[0068] As for an ink constituent, according to the desirable mode of this invention, it is desirable to come to contain sugar. As an example of a saccharide, a monosaccharide, a disaccharide, oligosaccharide (a trisaccharide and a tetrasaccharide are included), and polysaccharide are raised, and a glucose, a mannose, a fructose, a ribose, a xylose, arabinose, a galactose, an aldonic acid, a GURUSHI seal, a sorbitol, a maltose, a cellobiose, a lactose, a sucrose, a trehalose, a maltotriose, etc. are raised preferably. Here, polysaccharide means the sugar of a wide sense and suppose that it uses for the meaning containing the matter which exists in natures, such as an alginic acid, alpha-cyclodextrin, and a cellulose, widely.

[0069] Moreover, as a derivative of these saccharides, they are the reducing sugar (for example, sugar-alcohol (expressed with general formula HOCH₂n CH(OH)₂ OH (it is here and the integer of n=2-5 is expressed)), oxidation sugar, amino acid (for example, an aldonic acid, a uronic acid, etc.), a thiosugar, etc. are raised.) of said saccharide. Especially sugar-alcohol is desirable and a maltitol, a sorbitol, etc. are raised as an example.

[0070] the content of these saccharides — ink — 0.5 – 30% of the weight of the range is preferably suitable 0.1 to 40% of the weight In addition, you may add pH regulator, antiseptics, an antifungal agent, etc. if needed.

[0071] A drawing is used and explained to the ink-jet recording device which enforces the ink-jet record method by the ink-jet recording device this invention below an intermediary.

[0072] The ink-jet recording device of drawing 1 contains an ink constituent and reaction mixture on a tank, and is a mode by which an ink constituent and reaction mixture are supplied to a recording head through an ink tube. That is, a recording head 1 and the ink tank 2 are

opened for free passage by the ink tube 3. Here, it comes to divide the interior and, as for the ink tank 2, comes to prepare the room of two or more color ink constituents, and the room of reaction mixture by the ink constituent and the case.

[0073] A recording head 1 moves by the timing belt 6 driven by the motor 5 along with carriage 4. On the other hand, the paper 7 which is a record medium is put on the position which meets a recording head 1 by the platen 8 and the guide 9. In addition, in this mode, it comes to prepare a cap 10. A suction pump 11 is connected with this cap 10, and the so-called cleaning operation is performed. The attracted ink constituent is collected and put on the waste ink tank 13 through a tube 12.

[0074] The enlarged view of the nozzle side of a recording head 1 is shown in drawing 2. The portion shown by 1b is the nozzle side of reaction mixture, and it comes to prepare the nozzle 21 by which reaction mixture is breathed out in lengthwise. On the other hand, the portion shown by 1c is the nozzle side of an ink constituent, and a yellow ink constituent, a Magenta ink constituent, a cyano ink constituent, and a black ink constituent are breathed out from nozzles 22, 23, 24, and 25, respectively.

[0075] Furthermore, the ink-jet record method using the recording head of a publication is explained to this drawing 2 using drawing 3. A recording head 1 moves in the direction of arrow A. Between the movement, reaction mixture is breathed out from nozzle side 1b, and the band-like reaction mixture adhesion field 31 is formed on a record medium 7. Next, the specified quantity transfer of the record medium 7 is carried out at the direction arrow B of an ejection. A recording head 1 moves to Arrow A and an opposite direction all over drawing, and returns to the position at the left end of a record medium 7 in the meantime. And an ink constituent is printed to the reaction mixture adhesion field to which reaction mixture has already adhered, and a printing area 32 is formed in it.

[0076] Moreover, it is also possible to put in order and constitute all nozzles in a recording head 1 at a longitudinal direction like a publication in drawing 4. All over drawing, 41a and 41b are the **** nozzles of reaction mixture, and a ***** yellow ink constituent, a Magenta ink constituent, a cyano ink constituent, and a black ink constituent are breathed out from nozzles 42, 43, 44, and 45. The outward trip on which a recording head 1 goes and comes back to a carriage top in the recording head of such a mode, and a return trip -- also in any, it is a printable point and printing at a speed quicker than the case where the recording head shown in drawing 2 is used can be expected

[0077] By furthermore adjusting the surface tension of reaction mixture and an ink constituent as mentioned above preferably, irrespective of such adhesion sequence, quality printing is more fixed and is obtained. In this case, the regurgitation nozzle of reaction mixture can also be set to one (for example, the nozzle of 41b can be excluded all over drawing), and the miniaturization of the further head and improvement in the speed of printing can be attained.

[0078] Furthermore, there are some to which a supplement of an ink constituent is performed by exchanging the cartridge which is an ink tank in an ink-jet recording device. Moreover, this ink tank may be united with a recording head.

[0079] The desirable example of the ink-jet recording device using such an ink tank is shown in drawing 5. The same reference number was attached about the member same all over drawing as the equipment of drawing 1. In the mode of drawing 5, it comes to unite recording heads 1a and 1b with the ink tanks 2a and 2b. The regurgitation of an ink constituent and the reaction mixture shall be carried out for recording heads 1a or 1b, respectively. Printing method may be the same as that of the equipment of drawing 1 fundamentally. And in this mode, both recording head 1a, ink tank 2a [and], recording head 1a, and ink tank 2b move in a carriage 4 top.

[0080] Furthermore, the desirable example of the ink-jet recording device to which it comes to prepare the heater which heats the record medium with which printing was made is shown in drawing 6. Drawing 6 is the same as that of what was shown in drawing 1 except the point of having formed the heater 14. You may heat this heater 14, without contacting a record medium, such as irradiating infrared radiation etc. or spraying hot blast, even if it contacts a record medium and heats it.

[0081] You may be which mode of the method of making reaction mixture adhere only to the

place to which an ink constituent is made to adhere alternatively about adhesion in the record medium of reaction mixture, and the method of making reaction mixture adhere to the whole space. Although the former can hold down the consumption of reaction mixture to necessary minimum and is economical, a certain amount of precision is required of the position to which both reaction mixture and an ink constituent are made to adhere. On the other hand, although a demand of the precision of the adhesion position of reaction mixture and an ink constituent is eased for the latter compared with the former, a lot of reaction mixture is made to adhere to the whole space, and paper tends to curl in the case of dryness. Therefore, it may be determined in consideration of the combination of an ink constituent and reaction mixture whether to adopt which method. When adopting the former method, adhesion of reaction mixture can be based on the ink-jet record method.

[Example] Although the following examples explain this invention in detail below, this invention is not limited to these.

[0083] Ink A1 and A2 was prepared according to the conventional method in the reaction mixture A1 and A2 below Example A, and the row. That is, reaction mixture mixed the component shown below and was taken as reaction mixture. After the ink constituent distributed the coloring agent component with the dispersant component, other components were added, it mixed, and it filtered the insoluble element of the size more than fixed, and used it as the ink constituent.

[0084] Reaction mixture A1 magnesium nitrate and 6 hydrate The 25wt% triethylene-glycol monobutyl ether 10wt(s)% Glycerol 20wt(s)% Ion exchange water A residue Reaction mixture A2 A magnesium nitrate and 6 hydrate 25wt% Glycerol 20wt% Ion exchange water Residue [0085] Ink A1 pigment C.I pigment blue 15:3 8wt% solvent object A styrene-acrylic copolymer and ammonium salt 1.5wt% (molecular weight 7000, resinous principle 38wt%dispersant) gold [GURAN] -- PP-1000 7wt% (the Dainippon Ink make, a styrene-acrylic resin emulsion, 45% of resinous principles)

A malitol A 7wt% glycerol A 10wt%2-pyrrolidone 2wt% ion exchange water Residue Ink A2 pigment C.I pigment blue 15:3 3wt% solvent object A styrene-acrylic copolymer and ammonium salt 1.5wt% (molecular weight 7000, resinous principle 38wt%dispersant)

BONKOTO 5454 5wt% (the Dainippon Ink make, a styrene-acrylic resin emulsion, 45% of resinous principles)

Snow tex S 1.5wt% (the Nissan chemistry company make, colloidal silica, SiO2 content 30wt%) A malitol A 7wt% glycerol A 10wt%2-pyrrolidone 2wt% SAFI Norian 465 0.8wt% ion exchange water Residue [0086] The above reaction mixture and the surface tension of an ink constituent were as being shown in the following table [1st].

The 1st table surface tension (mN/m) reaction mixture A1 36.7 reaction mixture A2 50.2 ink A1 48.0 ink A2 33.0 [0088] With the combination of the reaction mixture not more than evaluation examination A1, and ink, it printed using ink jet printer MJ-700V2C. Reaction mixture was specifically printed by duty 100% on the recording paper shown below, and the ruled line pattern was printed in ink after that. The width of face of the obtained ruled line was measured.

[0089] In addition, it supposes that the weight of ink and reaction mixture is fixed at 0.05microg/dot, and ruled line width of face is the average of the evaluation paper 6 following paper.

Evaluation paper **Xerox P (Xerox Corp. make)

** Ricopy 6200 (Ricoh Co., Ltd. make)

** Xerox 4024 3R 721 (Xerox Corp. make)

** Neenah Bond (Kimberly Clark Corp. make)

** Xerox R (Xerox Corp. make)

** ***** (Honshu Paper Co., Ltd. make)

[0090] The result was as being shown in the following table [2nd].

[0091]

Table [2nd] [] reaction mixture Ink Average line breadth (micrometer) Example 1 A1 A2 110

Example 1 of comparison A1 A1 80 Example 2 of comparison A2 A1 65 Example 3 of comparison A2 A2 75 [0092] Example B Ink B1, B-2, and B3 and B4 were prepared by the same method as the above-mentioned example A in the following reaction mixture B1 and the row.

[0093]

Reaction mixture B1 A magnesium nitrate and 6 hydrate 25wt(s)% Triethylene-glycol monobutyl ether 10wt(s)% Glycerol 10wt(s)% SAFI Norian 465 1wt% SAFI Norian TG 1wt% Ion exchange water Residue [0094]

Ink B1 Pigment C.1 pigment blue 15:3 3wt% Solvent object A styrene-acrylic copolymer and ammonium salt 1.5wt% (molecular weight 7000, resinous principle 38wt%dispersant) BOKOTO 5454 5wt% (the Dainippon Ink (stock) make, a styrene-acrylic resin emulsion, 45% of resinous principles)

Snow tex S 1.5wt% (the product made from the Nissan chemistry, colloidal silica SiO2 content 30wt%)

A malitol 7wt(s)% Glycerol 10wt(s)% 2-pyrrolidone 2wt(s)% High tenor 325D 0.8wt% (the Dai-ichi Kogyo Seiyaku Co., Ltd. make, polyoxyethylene-alkyl-ether sodium-sulfate salt)

Ion exchange water Residue Ink B-2 Pigment C.1 pigment yellow 109 3wt% Pigment C.1 pigment yellow 110 0.5wt% Solvent object A styrene-acrylic copolymer and ammonium salt 1.5wt% (molecular weight 7000, resinous principle 38wt%dispersant)

BOKOTO 5454 5wt% (the Dainippon Ink (stock) make, a styrene-acrylic resin emulsion, 45% of resinous principles)

Snow tex S 1.5wt% (the product made from the Nissan chemistry, colloidal silica SiO2 content 30wt%)

A malitol 7wt(s)% Glycerol 10wt(s)% 2-pyrrolidone 2wt(s)% High tenor 325D 0.8wt% (the Dai-ichi Kogyo Seiyaku Co., Ltd. make, polyoxyethylene-alkyl-ether sodium-sulfate salt)

Ion exchange water Residue Ink B3 Pigment C.1 pigment red 122 3wt% Solvent object A styrene-acrylic copolymer and ammonium salt 1.5wt% (molecular weight 7000, resinous principle 38wt%dispersant)

BOKOTO 5454 5wt% (the Dainippon Ink (stock) make, a styrene-acrylic resin emulsion, 45% of resinous principles) Snow tex S 1.5wt% (the product made from the Nissan chemistry, colloidal silica SiO2 content 30wt%)

A malitol 7wt(s)% Glycerol 10wt(s)% 2-pyrrolidone 2wt(s)% High tenor 325D 0.8wt% (the Dai-ichi Kogyo Seiyaku Co., Ltd. make, polyoxyethylene-alkyl-ether sodium-sulfate salt)

Ion exchange water Residue Ink B4 Carbon black MA 7 5wt% Solvent object A styrene-acrylic copolymer and ammonium salt 1.5wt% (molecular weight 7000, resinous principle 38wt%dispersant)

BOKOTO 5454 5wt% (the Dainippon Ink (stock) make, a styrene-acrylic resin emulsion, 45% of resinous principles)

Snow tex S 1.5wt% (the product made from the Nissan chemistry, colloidal silica SiO2 content 30wt%)

A malitol 7wt(s)% Glycerol 10wt(s)% 2-pyrrolidone 2wt(s)% High tenor 325D 0.8wt% (the Dai-ichi Kogyo Seiyaku Co., Ltd. make, polyoxyethylene-alkyl-ether sodium-sulfate salt)

Ion exchange water Residue [0095] The above reaction mixture and the surface tension of an ink constituent were as being shown in the following table [3rd].

[0096]

The 3rd table surface tension (mN/m) reaction mixture B1 33.5 ink B1 37.0 ink B-2 38.6 ink B3 39.8 ink B4 38.2 [0097] Evaluation examination B1: Use measurement ink jet printer MJ-700V2C of the diameter of a dot, and it is 360 dot(s)/inch. By density, reaction mixture was printed by duty 100% on the recording paper shown below, it printed in ink after that, and the diameter of a dot was measured in accordance with the following error criteria.

[0098] In addition, the weight of ink and reaction of the evaluation paper 6 following paper.

fixed, the diameter of a dot is the average of the evaluation paper

*** Xerox P (Xerox Corp. make)

** Ricoh 6200 (Ricoh Co., Ltd. make)

** Xerox 4024 3R 721 (Xerox Corp. make)

** Neenah Bond (Kimberly Clark Corp. make)

** Xerox R (Xerox Corp. make)

** ***** (Honshu Paper Co., Ltd. make)

The diameter of A dot which the diameter of an error-criterion dot is 100 micrometers or more, and is high definition is 100 micrometers or less, and quality of image is poor B [0099]. The result was as being shown in the following table [4th].

[0100] Evaluation examination B-2: The stability of the evaluation ink B1-B4 of the stability of ink was evaluated as follows. That is, after sealing ink and leaving it under a condition (70 degree-Cx1 week and 70 degree-Cx2 week), change of a physical-properties value (viscosity, surface tension, pH value) and the generating situation of a foreign matter were observed. The result was evaluated in accordance with the following error criteria.

error-criterion [of 70 degrees C] x two-week neglect --- setting --- physical-properties value change and generating of a foreign matter --- nothing-A70-degree-Cx two-week neglect --- setting --- physical-properties value change or the B70-degree-Cx one-week neglect with generating of a foreign matter --- setting --- : physical-properties value change or with [of a foreign matter] generating --- NG [0101] The result was as being shown in the following table [4th].

[0102]

the 4th table [] Ink Diameter of a dot (micrometer) Evaluation of the diameter of a dot Stability of ink B1 119 A Ink B-2 128 A Ink B3 108 A Ink B4 122 A A [0103] Ink C1, C2, C3,

and C4 was prepared by the same method as the above-mentioned example A in the reaction mixture C1 below Example C, and the row.

[0104]

Reaction mixture C1 A magnesium nitrate and 6 hydrate 25wt(s)% Triethylene-glycol monobutyl ether 10wt(s)% Glycerol 10wt(s)% SAFI Norian 465 1wt% SAFI Norian TG 1wt% Ion exchange water Residue [0105]

Ink C1 Pigment C.1 pigment blue 15:3 3wt% Solvent object A styrene-acrylic copolymer and ammonium salt 1.5wt% (molecular weight 7000, resinous principle 38wt%dispersant)

BOKOTO 5454 5wt% (the Dainippon Ink make, a styrene-acrylic resin emulsion, 45% of resinous principles)

Snow tex S 1.5wt% (the product made from the Nissan chemistry, colloidal silica SiO2 content 30wt%)

A malitol 7wt(s)% Glycerol 10wt(s)% 2-pyrrolidone 2wt(s)% High tenor 325D 0.8wt% (Dai-ichi Kogyo Seiyaku Co., Ltd., polyoxyethylene-alkyl-ether sodium-sulfate salt)

Ion exchange water Residue Ink C2 Pigment C.1 pigment yellow 109 3wt% Pigment C.1 pigment yellow 110 0.5wt% Solvent object A styrene-acrylic copolymer and ammonium salt 1.5wt% (molecular weight 7000, resinous principle 38wt%dispersant)

BOKOTO 5454 5wt% (the Dainippon Ink make, a styrene-acrylic resin emulsion, 45% of resinous principles)

Snow tex S 1.5wt% (the product made from the Nissan chemistry, colloidal silica SiO2 content 30wt%)

A malitol 7wt(s)% Glycerol 10wt(s)% 2-pyrrolidone 2wt(s)% High tenor NE-15 0.8wt% (Dai-ichi Kogyo Seiyaku Co., Ltd., polyoxyethylene-alkyl-phenyl-ether sulfuric-acid ammonium salt)

Ion exchange water Residue Ink C3 Pigment C.1 pigment red 122 3wt% Solvent object A styrene-acrylic copolymer and ammonium salt 1.5wt% (molecular weight 7000, resinous principle 38wt%dispersant)

BOKOTO 5454 5wt% (the Dainippon Ink make, a styrene-acrylic resin emulsion, 45% of resinous principles)

Snow tex S 1.5wt% (the product made from the Nissan chemistry, colloidal silica SiO2 content 30wt%)

A malitol 7wt(s)% Glycerol 10wt(s)% 2-pyrrolidone 2wt(s)% Neo gene S-20 0.8wt% (Dai-ichi Kogyo Seiyaku Co., Ltd., straight chain sodium dodecylbenzenesulfonate salt)

Ion exchange water Residue Ink C4 Carbon black MA 7 5wt% Solvent object A styrene-acrylic copolymer and ammonium salt 1.5wt% (molecular weight 7000, resinous principle

38wt%dispersant)
 BONKOTO 5454 5wt% (the Dainippon Ink make, a styrene-acrylic resin emulsion, 45% of resinous principles)
 Snow tex S 1.5wt% (the product made from the Nissan chemistry, colloidal silica SiO2 content 30wt%)
 A maltitol 7wt(s)% Glycerol 10wt(s)% 2-pyrrolidone 2wt(s)% Neocol SW 0.8wt% (Dai-Ichi Kogyo Seiyaku Co., Ltd., dialkyl sulfo succinate sodium salt)
 Ion exchange water Residue [0106] The above reaction mixture and the surface tension of an ink constituent were as being shown in the following table [5th].
 [0107]
 The 5th table surface tension (mN/m) reaction mixture C1 33.5 ink C1 37.0 ink C2 37.6 ink C3 38.9 ink C4 32.7 [0108] Evaluation examination C1: Ink C1-C4 was followed at the above-mentioned reaction mixture C1 row in the measurement evaluation examination B1 of the diameter of a dot, and the same examination. The result was as being shown in the following table [6th].
 [0109] Evaluation examination C2: The above-mentioned ink C1-C4 was followed in the same examination as evaluation examination B-2 of the stability of ink. The result was as being shown in the following table [6th].
 [0110]
 the 6th table [] Ink Diameter of a dot (micrometer) Evaluation of the diameter of a dot Stability of ink Ink C1 106 A Ink C2 118 A A Ink C3 112 A A Ink C4 122 A A
 [Translation done.]

*** NOTICES ***

Japan Patent Office is not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.*** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is drawing showing the ink-jet recording device preferably used for operation of the ink-jet record method by this invention, and, as for an ink constituent and reaction mixture, a recording head and an ink tank are supplied to a recording head with an ink tube in this mode coming independently, respectively.

[Drawing 2] It is the enlarged view of the nozzle side of a recording head, 1b is the nozzle side of reaction mixture, and 1c is the nozzle side of an ink constituent.

[Drawing 3] It is drawing explaining the ink-jet record method using the recording head of drawing 2. All over drawing, 31 are a reaction mixture adhesion field, and 32 is the printing area where it adhered to reaction mixture upwards, and the ink constituent was printed.

[Drawing 4] It is drawing showing mode with the another recording head preferably used for operation of the ink-jet record method by this invention, and all regurgitation nozzles arrange in a longitudinal direction, and are constituted.

[Drawing 5] It is drawing showing the ink-jet recording device preferably used for operation of the ink-jet record method by this invention, and comes to unify a recording head and an ink tank in this mode.

[Drawing 6] It is drawing showing the ink-jet recording device preferably used for operation of the ink-jet record method by this invention, and comes to have the heater which heats the record medium after printing in this mode.

[Description of Notations]

- 1 Recording Head
- 2 Ink Tank
- 3 Ink Tube
- 14 Heater
- 21 Reaction Mixture Regurgitation Nozzle
- 22, 23, 24, 25 Ink constituent regurgitation nozzle
- 31 Reaction Mixture Adhesion Field
- 32 Printing Area

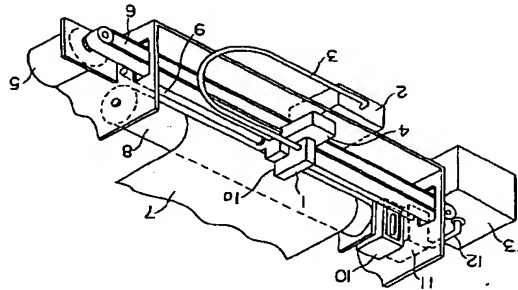
[Translation done.]

特許請求の範囲		特許請求の範囲	
(51)IntCl ⁴	印刷記号	F I	
C09 J 11/00		C09 J 11/00	
B41 J 2/01		B41 M 5/00	A
B41 M 5/00		B41 J 3/04	E
			1.01 Y
審査請求 未請求 請求項の数11 O L (全 15頁)			
(21)出願番号	特開平9-249119	(71)出願人	00000208 セイコーエプソン株式会社
(22)出願日	平成9年(1997)9月12日		東京都新宿区西新宿2丁目4番1号
(31)優先権主張番号	特開平8-256332	(72)発明者	加藤 真一 長野県諏訪市大和三丁目3番5号
(32)優先日	平8(1996)9月27日		セイコ エプソン株式会社内
(33)優先権主張国	日本 (J P)	(72)発明者	竹本 清彦 長野県諏訪市大和三丁目3番5号
(31)優先権主張番号	特開平8-30227		セイコ エプソン株式会社内
(32)優先日	平8(1996)11月13日	(72)発明者	和田 和英 長野県諏訪市大和三丁目3番5号
(33)優先権主張国	日本 (J P)		セイコ エプソン株式会社内
(34)代理人	弁護士 佐藤 一雄 (外2名)		

(54)【発明の名称】 インクジェット記録方法

(57)【要約】
【課題】 記録媒体に、反応液とインク組成物を用いて印字を行うインクジェット記録方法において、良好な画像が得られる方法の提供。

【解決手段】 着色剤、樹脂エマルジョンなどを含んだインク組成物と、この着色剤、樹脂エマルジョンなどの成分と反応して凝集物を生成する多価金属塩、ポリアルミンなどの反応剤を含んだ反応液であって、反応液およびインク組成物の表面張力がともに40mN/m未満のものを用いる。また、この表面張力を具現するために、アニオン性界面活性剤である、ポリオキシエレンアルキルエーテル硫酸塩のナトリウム塩を用いる。



(2) 特開平10-195404
2
本発明は、インクジェット記録方法に関し、詳しくは記録媒体に反応液とインク組成物とを付着させて印字を行うインクジェット記録方法に関する。

【0002】背景技術
インクジェット記録方法は、インク組成物の小滴を飛翔させ、紙等の記録媒体に付着させて印字を行う印刷方法である。この方法は、比較的安価な装置で高解像度、高品位な画像を、高速で印刷可能であるという特徴を有する。通常インクジェット記録に使用されるインク組成物は、水を主成分とし、これに着色成分および自粘り防止等の目的でグリセリン等の潤滑剤を含有したものが一般的である。

【0003】一方、インクジェット記録方法として、最近新たに、多価金属塩溶液を記録媒体に適用した後、少なくとも一つのカルボキシル基を有する染料を含むインク組成物を適用する方法が提案されている(例えば、特開平5-202328号公報)。この方法においては、多価金属イオンと染料から不溶性複合体が形成され、この複合体の存在により、雨水性があつかうカラーブリードがない高品位の画像を得ることができるとされている。

【0004】また、少なくとも浸透性を付与する界面活性剤または浸透性溶剤および塩を含有するカラーインクと、この塩と作用により増粘または凝集するブラックインクとを組合せて使用することにより、画像濃度が高かつカラーブリードがない高品位のカラー画像が得られるという提案もなされている(特開平6-106735号公報)。すなわち塩を含んだ第一の液と、インク組成物との二液を印字することで、良好な画像が得られるとするインクジェット記録方法が提案されている。

【0005】また、その他にも二液を印字するインクジェット記録方法が提案されている(例えば、特開平3-240557号公報、特開平3-240558号公報)。

【0006】本発明者等は、今般、このような二液を印字するインクジェット記録方法において、反応液とインク組成物との表面張力をともに40mN/m未満とするすることで、良好な印字が実現できるとの知見を得た。本発明はかかる知見に基づいたものである。

【0007】従って、本発明は、二液を印字するインクジェット記録方法において、良好な画像が実現できる方法の提供をその目的としている。

【0008】そして、本発明によるインクジェット記録方法は、記録媒体に、反応剤を含んだ反応液とインク組成物とを付着させて、印字を行うインクジェット記録方法であって、前記反応液および前記インク組成物としてその表面張力がともに40mN/m未満のものを用いるもの、である。

50 【0009】

【0083】実施例A

以下の反応液A1およびA2、ならびにインクA1およびA2を常法に従い調製した。即ち、反応液は、下記に示す成分を混合して、反応液とした。インク組成物は、* 【0084】

反応液A1	
硝酸マグネシウム・六水和物	25wt%
トリエチレングリコールモノブチルエーテル	10wt%
グリセリン	20wt%
イオン交換水	残量
反応液A2	
硝酸マグネシウム・六水和物	25wt%
グリセリン	20wt%
イオン交換水	残量

【0085】

インクA1	
顔料 C. I.ピグメントブルー15:3	8wt%
液媒体	
スチレン-アクリル共重合体・アンモニウム塩 (分子量7000、樹脂成分38wt%:分散剤)	1.5wt%
グラントールPP-1000 (大日本インキ(株)製、スチレン-アクリル樹脂エマルジョン、樹脂成分45%)	7wt%
マルチトール	7wt%
グリセリン	10wt%
2-ピロリドン	2wt%
イオン交換水	残量
インクA2	
顔料 C. I.ピグメントブルー15:3	3wt%
液媒体	
スチレン-アクリル共重合体・アンモニウム塩 (分子量7000、樹脂成分38wt%:分散剤)	1.5wt%
ボンコート5454 (大日本インキ(株)製、スチレン-アクリル樹脂エマルジョン、樹脂成分45%)	5wt%
スノーデックスS	1.5wt%
(日産化学社製、コロイダルシリカ、 SiO_2 含有量30wt%)	
マルチトール	7wt%
グリセリン	10wt%
2-ピロリドン	2wt%
サーフイノール465	0.8wt%
イオン交換水	残量

【0086】以上の反応液およびインク組成物の表面張力は、以下の第1表に示される通りであった。

【0087】第1表

表面張力 (mN/m)

反応液A1 36.7

反応液A2 50.2

インクA1 48.0

50 【0089】なお、インクおよび反応液の重量は0.0

5 $\mu\text{g}/\text{dot}$ で一定とし、露光後は下記の露光紙六紙の平均値である。

評価紙

- ①Xerox P (ゼロックス(株)製)
②Ricopy 6200 (リコー(株)製)
③Xerox 4024 3R 721 (ゼロックス(株)製) *

【0090】結果は、以下の第2表に示される通りであった。

第2表		
反応液	インク	平均線幅 (μm)
実施例1	A1 A2	110
比較例1	A1 A1	80
比較例2	A2 A1	65
比較例3	A2 A2	75

【0092】実施例B 以下の反応液B1、ならびにインクB1、B2、B3およびB4を上記実施例Aと同様

反応液B1	
硝酸マグネシウム・六水和物	25wt%
トリエチレングリコールモノブチルエーテル	10wt%
グリセリン	10wt%
サーフイノール465	1wt%
サーフイノールTG	1wt%
イオン交換水	残量

【0094】

インクB1	
顔料C. I. ピグメントブルー15:3	3wt%
液媒体	
スチレン-アクリル共重合体・アンモニウム塩 (分子量7000、樹脂成分38wt%:分散剤)	1.5wt%
ボンコート5454 (大日本インキ(株)製、スチレン-アクリル樹脂エマルジョン、樹脂成分45%)	5wt%
スノーデックスS	1.5wt%
(日産化学社製、コロイダルシリカ SiO_2 含有量30wt%)	
マルチトール	7wt%
グリセリン	10wt%
2-ピロリドン	2wt%
ハイテノール325D (第一工業製薬(株)製、ポリオキシエチレンアルキルエーテル硫酸ナトリウム塩)	0.8wt%
イオン交換水	残量
インクB2	
顔料C. I. ピグメントイエロー109	0.5wt%
液媒体	
スチレン-アクリル共重合体・アンモニウム塩 (分子量7000、樹脂成分38wt%:分散剤)	1.5wt%
ボンコート5454 (大日本インキ(株)製、スチレン-アクリル樹脂エマルジョン、樹脂成分45%)	5wt%
スノーデックスS	1.5wt%

(日産化学製、コロイダルシリカSiO₂含有量30wt%)
マルチートール 7wt%
グリセリン 10wt%
2-ピロリドン 2wt%
ハイテノール325D 0.8wt%
(第一工業製薬(株)製、ポリオキシエチレンアルキルエーテル硫酸ナトリウム塩)

イオン交換水 残量
インクB3 3wt%
原料C. I. ビグメントレッド122 1.5wt%
液媒体 スチレン-アクリル共重合体・アンモニウム塩 (分子量7000、樹脂成分38wt%:分散剤)
ボンコート5454 5wt%
(大日本インキ(株)製、スチレン-アクリル樹脂エマルジョン、樹脂成分45%)

スノーデックスS 1.5wt%
(日産化学製、コロイダルシリカSiO₂含有量30wt%)
マルチートール 7wt%
グリセリン 10wt%
2-ピロリドン 2wt%
ハイテノール325D 0.8wt%
(第一工業製薬(株)製、ポリオキシエチレンアルキルエーテル硫酸ナトリウム塩)

イオン交換水 残量
インクB4 5wt%
カーボンブラックMA7 1.5wt%
液媒体 スチレン-アクリル共重合体・アンモニウム塩 (分子量7000、樹脂成分38wt%:分散剤)
ボンコート5454 5wt%
(大日本インキ(株)製、スチレン-アクリル樹脂エマルジョン、樹脂成分45%)

スノーデックスS 1.5wt%
(日産化学製、コロイダルシリカSiO₂含有量30wt%)
マルチートール 7wt%
グリセリン 10wt%
2-ピロリドン 2wt%
ハイテノール325D 0.8wt%
(第一工業製薬(株)製、ポリオキシエチレンアルキルエーテル硫酸ナトリウム塩)

イオン交換水 残量
インクB3 39.8
インクB4 38.2

[0097] 評価試験B1: ドット径の測定

インクジェットプリンターMJ-700V2Cを用いてインクジェットプリンターMJ-700V2Cを用いて360dot/inchの密度で、以下に示す記録紙に反応液を10% dutyで印字し、その後インクにより印字を行い、以下の評価基準に従いドット径を測定した。
50 [0098] なお、インクおよび反応液の重量は0.0

5μg/dotで一定とし、ドット径は下記の評価紙六枚の平均値である。

評価紙
①Xerox P (ゼロックス(株)製)
②Ricopy 6200 (リコー(株)製)
③Xerox 4024 3R 721 (ゼロックス(株)製)
④Neonah Bond (キンバリークラーク社製)
⑤Xerox R (ゼロックス(株)製)
⑥やまゆり (本州製紙(株)製)

評価基準
ドット径は100μm以上であり、高画質である: A
ドット径は100μm以下であり、画質は不良である: R
[0099] 結果は、以下の第4表に示される通りであった。
[0100] 評価試験B2: インクの安定性の評価 *

第4表

インク	ドット径(μm)	ドット径の評価	インクの安定性
インクB1	119	A	A
インクB2	128	A	A
インクB3	108	A	A
インクB4	122	A	A

[0103] 実験例C
以下の反応液C1、ならびにインクC1、C2、C3および[0104]

反応液C1
硝酸マグネシウム・六水和物 25wt%
トリエチレングリコールモノブチルエーテル 10wt%
グリセリン 10wt%
サーフイノール465 1wt%
サーフイノールTG 1wt%
イオン交換水 残量

[0105]

インクC1
原料C. I. ビグメントブルー15:3 3wt%
液媒体
スチレン-アクリル共重合体・アンモニウム塩 1.5wt%
(分子量7000、樹脂成分38wt%:分散剤)
ボンコート5454 5wt%
(大日本インキ(株)製、スチレン-アクリル樹脂エマルジョン、樹脂成分45%)
スノーデックスS 1.5wt%
(日産化学製、コロイダルシリカSiO₂含有量30wt%)
マルチートール 7wt%
グリセリン 10wt%
2-ピロリドン 2wt%
ハイテノール325D 0.8wt%
(第一工業製薬(株)製、ポリオキシエチレンアルキルエーテル硫酸ナトリウム塩)
イオン交換水 残量
インクC2

[0095] 以上の反応液およびインク組成物の表面張力は、以下の第3表に示される通りであった。

[0096]

第3表

表面張力(mN/m)
反応液B1 33.5
インクB1 37.0
インクB2 38.6

23

原料C、I、ビグメントイエロー109

原料C、I、ビグメントイエロー110

液媒体

ステレン-アクリル共重合体・アンモニウム塩

(分子量7000、樹脂成分38wt%：分散剤)

ボニコート5454

(大日本インキ(株)製、ステレン-アクリル樹脂エマルジョン、

樹脂成分45%)

スノーデックスS

(日産化学製、コロイダルシリカSiO₂含有量30wt%)

マルチトール

グリセリン

2-ヒロリドン

ハイテナーNE-15

(第一工業製薬(株)、ポリオキシエチレンアルキルフェニルエーテル硫酸

アンモニウム塩)

イオン交換水

インクC3

原料C、I、ビグメントレッド122

液媒体

ステレン-アクリル共重合体・アンモニウム塩

(分子量7000、樹脂成分38wt%：分散剤)

ボニコート5454

(大日本インキ(株)製、ステレン-アクリル樹脂エマルジョン、

樹脂成分45%)

スノーデックスS

(日産化学製、コロイダルシリカSiO₂含有量30wt%)

マルチトール

グリセリン

2-ヒロリドン

オオグンS-20

(第一工業製薬(株)、直鎖ドデシルベンゼンホルホン酸ナトリウム塩)

イオン交換水

インクC4

カーボンブラックMA7

液媒体

ステレン-アクリル共重合体・アンモニウム塩

(分子量7000、樹脂成分38wt%：分散剤)

ボニコート5454

(大日本インキ(株)製、ステレン-アクリル樹脂エマルジョン、

樹脂成分45%)

スノーデックスS

(日産化学製、コロイダルシリカSiO₂含有量30wt%)

マルチトール

グリセリン

2-ヒロリドン

ネオコールSW

(第一工業製薬(株)、ジアルキルホルホン硫酸エステルナトリウム塩)

イオン交換水

残量

5wt%

1.5wt%

7wt%

10wt%

2wt%

0.8wt%

3wt%

1.5wt%

5wt%

7wt%

10wt%

2wt%

25

[0107]

第5表

表面張力値 (mN/m)

反応液C1 33.5

インクC1 37.0

インクC2 37.6

インクC3 38.9

インクC4 32.7

[0108] 評価試験C1：ドット径の測定

第6表

インク

ドット径 (μm)

インクC1 106

インクC2 118

インクC3 112

インクC4 122

インクC1 106

インクC2 118

インクC3 112

インクC4 122

インクC1 106

インクC2 118

インクC3 112

インクC4 122

インクC1 106

インクC2 118

インクC3 112

インクC4 122

インクC1 106

インクC2 118

インクC3 112

インクC4 122

インクC1 106

インクC2 118

インクC3 112

インクC4 122

インクC1 106

インクC2 118

インクC3 112

インクC4 122

インクC1 106

インクC2 118

インクC3 112

インクC4 122

インクC1 106

インクC2 118

インクC3 112

インクC4 122

インクC1 106

インクC2 118

インクC3 112

インクC4 122

インクC1 106

インクC2 118

インクC3 112

インクC4 122

インクC1 106

インクC2 118

インクC3 112

インクC4 122

インクC1 106

インクC2 118

(14)

25

[0107]

第5表

表面張力値 (mN/m)

反応液C1 33.5

インクC1 37.0

インクC2 37.6

インクC3 38.9

インクC4 32.7

[0108] 評価試験C1：ドット径の測定

第6表

インク

ドット径 (μm)

インクC1 106

インクC2 118

インクC3 112

インクC4 122

インクC1 106

インクC2 118

インクC3 112

インクC4 122

インクC1 106

インクC2 118

インクC3 112

インクC4 122

インクC1 106

インクC2 118

インクC3 112

インクC4 122

インクC1 106

インクC2 118

インクC3 112

インクC4 122

インクC1 106

インクC2 118

インクC3 112

インクC4 122

インクC1 106

インクC2 118

インクC3 112

インクC4 122

インクC1 106

インクC2 118

インクC3 112

インクC4 122

インクC1 106

インクC2 118

インクC3 112

インクC4 122

インクC1 106

インクC2 118

インクC3 112

インクC4 122

インクC1 106

インクC2 118

インクC3 112

インクC4 122

インクC1 106

インクC2 118

インクC3 112

インクC4 122

インクC1 106

インクC2 118

特開平10-195404

25

[0107]

第5表

表面張力値 (mN/m)

反応液C1 33.5

インクC1 37.0

インクC2 37.6

インクC3 38.9

インクC4 32.7

[0108] 評価試験C1：ドット径の測定

第6表

インク

ドット径 (μm)

インクC1 106

インクC2 118

インクC3 112

インクC4 122

インクC1 106

インクC2 118

インクC3 112

インクC4 122

インクC1 106

インクC2 118

インクC3 112

インクC4 122

インクC1 106

インクC2 118

インクC3 112

インクC4 122

インクC1 106

インクC2 118

インクC3 112

インクC4 122

インクC1 106

インクC2 118

インクC3 112

インクC4 122

インクC1 106

インクC2 118

インクC3 112

インクC4 122

インクC1 106

インクC2 118

インクC3 112

インクC4 122

インクC1 106

インクC2 118

インクC3 112

インクC4 122

インクC1 106

インクC2 118

インクC3 112

インクC4 122

インクC1 106

インクC2 118

インクC3 112

インクC4 122

インクC1 106

インクC2 118

インクC3 112

インクC4 122

インクC1 106

インクC2 118

特開平10-195404

24

原料C、I、ビグメントイエロー109

原料C、I、ビグメントイエロー110

液媒体

ステレン-アクリル共重合体・アンモニウム塩

(分子量7000、樹脂成分38wt%：分散剤)

ボニコート5454

(大日本インキ(株)製、ステレン-アクリル樹脂エマルジョン、

樹脂成分45%)

スノーデックスS

(日産化学製、コロイダルシリカSiO₂含有量30wt%)

マルチトール

グリセリン

2-ヒロリドン

ハイテナーNE-15

(第一工業製薬(株)、ポリオキシエチレンアルキルフェニルエーテル硫酸

アンモニウム塩)

イオン交換水

インクC3

原料C、I、ビグメントレッド122

液媒体

ステレン-アクリル共重合体・アンモニウム塩

(分子量7000、樹脂成分38wt%：分散剤)

ボニコート5454

(大日本インキ(株)製、ステレン-アクリル樹脂エマルジョン、

樹脂成分45%)

スノーデックスS

(日産化学製、コロイダルシリカSiO₂含有量30wt%)

マルチトール

グリセリン

2-ヒロリドン

オオグンS-20

(第一工業製薬(株)、直鎖ドデシルベンゼンホルホン酸ナトリウム塩)

イオン交換水

インクC4

カーボンブラックMA7

液媒体

ステレン-アクリル共重合体・アンモニウム塩

(分子量7000、樹脂成分38wt%：分散剤)

ボニコート5454

(大日本インキ(株)製、ステレン-アクリル樹脂エマルジョン、

樹脂成分45%)

スノーデックスS

(日産化学製、コロイダルシリカSiO₂含有量30wt%)

マルチトール

グリセリン

2-ヒロリドン

ネオコールSW

(第一工業製薬(株)、ジアルキルホルホン硫酸エステルナトリウム塩)

イオン交換水

残量

5wt%

1.5wt%

7wt%

10wt%

2wt%

0.8wt%

3wt%

1.5wt%

5wt%

7wt%

10wt%

2wt%

(14)

25

[0107]

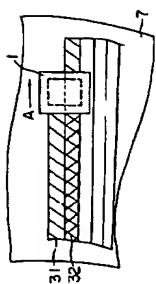
第5表

表面張力値 (mN/m)

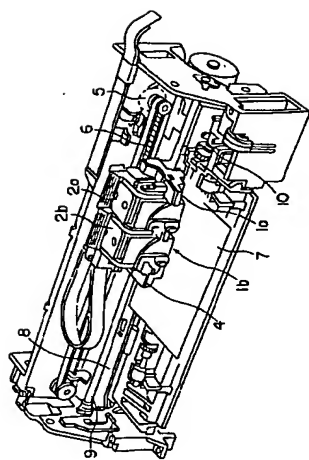
反応液C1 33.5

インクC1 37.

【图 3】



【图 5】



【图 6】

